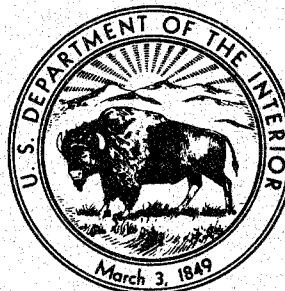


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Development of Modified Polyolefin Membranes for Reverse Osmosis

United States Department of the Interior



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Development of Modified Polyolefin Membranes for Reverse Osmosis

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UNITED STATES DEPARTMENT OF THE INTERIOR • Walter J. Hickel, Secretary
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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

ACKNOWLEDGEMENTS

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I. SUMMARY

Procedures for the radiation induced grafting of polyethylene film which yield a variety of modified polyethylene membranes have been established. Modification of the polyethylene was accomplished by grafting with acidic monomers such as acrylic and methacrylic acids, basic monomers such as aminoalkyl methacrylates and vinylpyridines, and neutral monomers such as hydroxyalkyl methacrylates. Some graft terpolymers were prepared by incorporating relatively hydrophobic monomers such as acrylonitrile, acrylamide, or vinyl acetate into the grafting solution along with acrylic acid. Crosslinking during grafting was accomplished by use of difunctional monomers in the grafting solution.

The membranes so produced maintained much of the tensile strength and elongation of the original polyethylene. The acid- and base-grafted films were hydrophilic, particularly as the potassium and hydrochloride salts, respectively. The hydrophilicity of such membranes was reduced by crosslinking or by cograftering with a hydrophobic monomer. The neutral membranes appeared to be relatively impermeable to water. The degree of grafting of acrylic acid-grafted membranes was found to be a linear function of the acrylic acid concentration in the grafting solution at the radiation dose rates and total dose used. Grafting was uniform on films of 25 feet in length. Chain length of the pendant graft polymer chains was varied by varying the concentration of chain terminator in the grafting solution.

The hydrophilic acid- and base-grafted membranes swell reversibly on wetting. They appear to lose some imbibed water under hydraulic pressure, which reduces the rate of water and salt transport across the grafted membrane, as evidenced by a decrease in the membrane constant A and an enhanced salt rejection. The loss of imbibed water with pressure increase was found to be reversible.

The equilibrium water concentration of acrylic acid-grafted films was shown to be a linear function of the degree of grafting, as was water transport. It appeared that water transport through these films was by viscous flow, and salt transport was strongly coupled to

water transport. Salt rejection appeared to be due to simple ion exclusion, divalent coions being more highly rejected than monovalent coions.

The acrylic acid-grafted membranes were found to be thermally sensitive. Heating in air above 100°C or in boiling toluene decreased water flux and increased salt rejection, while heating in water above 100°C led to increases in water flux and decreases in salt rejection.

Various attempts were made to improve the performance of grafted films by reducing their hydrophilicity. Conversion of an acrylic acid-grafted film to the copper salt led to a large increase in water flux, but the salt rejection fell to a low value. Reaction of an acrylic acid-grafted film with a solution of poly(4-vinylpyridine) to form a surface polysalt layer produced a film of improved salt rejection but with reduced flux.

Inclusion of either hydrophobic monomers or difunctional crosslinking agents in the grafting solution along with acrylic acid produced membranes with improved salt rejection and low water flux.

II. INTRODUCTION

As part of a project for the Jet Propulsion Laboratory to develop a sterilizable battery separator for silver-zinc batteries, a process for the modification of polyethylene film involving grafting with acrylic acid followed by crosslinking using divinylbenzene was developed. Both reactions were initiated by radiation from a cobalt-60 source.

Application of the above process to modification of polyethylene films with other monomers capable of free radical polymerization was undertaken with the goal of developing a membrane suitable for desalination of sea or brackish water by reverse osmosis.

The purpose of the experimental program was to produce modified polyolefin membranes with good physical and chemical stability, high salt rejection and high flux. The approaches to be considered for accomplishing these objectives involved modification of polyolefin films and hollow fibers by radiation grafting with acidic materials, basic materials, and mixtures of acidic and basic materials.

A preliminary screening study was conducted to determine the effect of the monomers used to modify polyethylene on water flux and salt rejection. Membranes prepared by grafting polyethylene with acrylic acid or mixtures of acrylic acid and other monomers showed the most promise, with water fluxes of 2 to 8 gfd and salt rejections of 50 to 80 percent at 400 psig with 0.25 wt % saline feed. However, the membranes were very hydrophilic and were highly swollen when wet. Salt and water transport were highly coupled, presumably due to the large amount of water in the swollen membranes.

It was shown that, for acrylic acid-grafted films, salt and water transport properties were independent of polymer side chain length at a given degree of grafting. It was also shown that the degree of grafting of polyethylene could be controlled by adjusting the acrylic acid concentration in the grafting solution. Means were sought to limit the hydrophilicity of the acrylic acid-grafted films. Thermal treatment in aqueous media led to enhanced swelling with

increased flux and loss of salt rejection, while thermal treatment in air led to loss of flux.

Conversion of the films to their cupric salts in order to induce ionic crosslinks failed to give tighter membranes. Large flux increases and very low salt rejections were obtained.

Attempts to limit the hydrophilicity and reduce the swelling of wet films were made utilizing graft copolymers in which mixtures of hydrophilic and hydrophobic monomers were grafted onto polyethylene. Also, further chemical modification of grafted films was undertaken in attempts to improve salt rejection.

III. EXPERIMENTAL PROCEDURES

A. Procedure for Irradiation Grafting Polyolefin Films

A desired length of the polyolefin film is backed with absorbent crepe paper toweling or cheesecloth and is rolled onto a one-quarter inch aluminum pipe which is capped at one end. In screening runs, the length of film used is five feet. Twenty-five foot lengths are also prepared of films which show promise, to provide larger quantities of film for evaluation.

The roll of film and backing material is placed in a suitable size hydrometer jar (38 mm x 357 mm for five-foot rolls; 75 mm x 550 mm for twenty-five foot rolls). For the small rolls, the aluminum pipe is removed prior to placing in the jar, while the pipe is left in the larger rolls. The hydrometer jar is then closed with a rubber stopper fitted with inlet and outlet tubes which can be sealed with vacuum tubing and screw clamps. The hydrometer jar is connected to a vacuum system and pumped down to ca. 2 mm Hg to remove oxygen. The jar is backflushed with nitrogen and again evacuated.

A grafting solution of the desired monomer in a suitable solvent is drawn into the evacuated jar. During screening runs, the grafting solution usually contains twenty-five percent monomer by weight. Solvents used are usually benzene, methanol or water, depending upon the solubility properties of the monomer. The filled hydrometer jar is alternately evacuated and pressured with nitrogen several times to remove air entrapped in the roll, and the inlet and outlet tubes are sealed. The filled jars are allowed to stand for at least 24 hours to provide time for the film to equilibrate with the grafting solution.

The jars are placed on turntables in the irradiation facility and are exposed to a uniform cobalt-60 source adjusted to give a dose rate of 0.012 megarad per hour until a total dose of 0.815 megarad has been applied. The hydrometer jars are rotated during the irradiation period in order to apply a uniform radiation dose to the film.

The irradiation tables are constructed so that eight samples can be run simultaneously under equivalent conditions. In Figure 1 can be seen eight five-foot rolls of film ready for grafting, while Figure 2 shows eight twenty-five foot rolls on the irradiation table. The primary difference is that the twenty-five foot rolls still contain the aluminum pipe down the center of the roll, and this pipe is utilized as a thermocouple well so that the temperature of the film roll can be monitored continuously during the grafting. Temperature readings are recorded on an eight-point recorder.

After completion of the irradiation period, the jars are removed from the radiation facility and allowed to stand for 24 hours in order to permit reaction of the remaining active sites.

The film is removed from the jar, unrolled, and separated from the paper toweling or cheesecloth. The film is then washed in solvents suitable for removing homopolymer which may be deposited on the film and allowed to dry on paper toweling.

B. Irradiation Configuration and Dosimetry

Irradiation of the polyethylene rolls is carried out in Southwest Research Institute's Radiation Effects Facility. The radiation source consists of approximately 10,000 curies of high specific activity cobalt-60. The cobalt-60 sources are individually encapsulated in stainless tapes $1\frac{1}{2}'' \times 2'' \times \frac{1}{8}''$. To provide a uniform radiation field wide enough for eight samples and high enough to cover the large rolls, the individual cobalt-60 tapes are evenly spaced on the center line of a vertical semiparabolic holder, which is mounted on a remotely controlled dolly.

Mapping the gamma flux in the target area (front) of the source indicated workable isodose volumes of 20,000 rads sufficient to contain eight turntables and target cylinders. This volume was almost semicircular and symmetrical about the center line of the source, with the center cylinders offset slightly farther from the source. The target arrangement is shown in Figures 1 and 2.

Detailed dosimetry using the Bausch and Lomb cobalt glass chip technique was performed on the irradiation tables and large

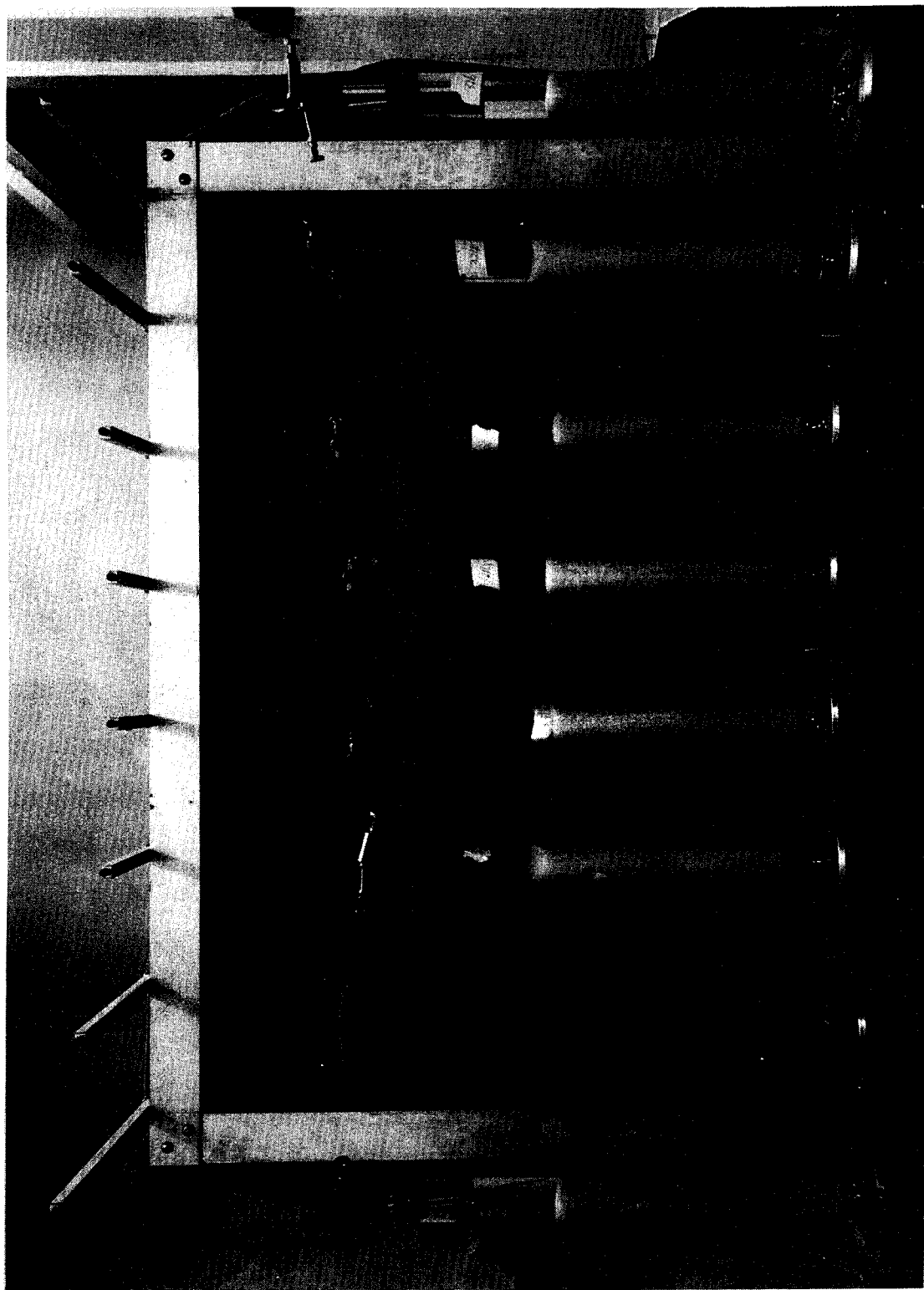


FIGURE 1. IRRADIATION TABLE, FIVE-FOOT ROLLS

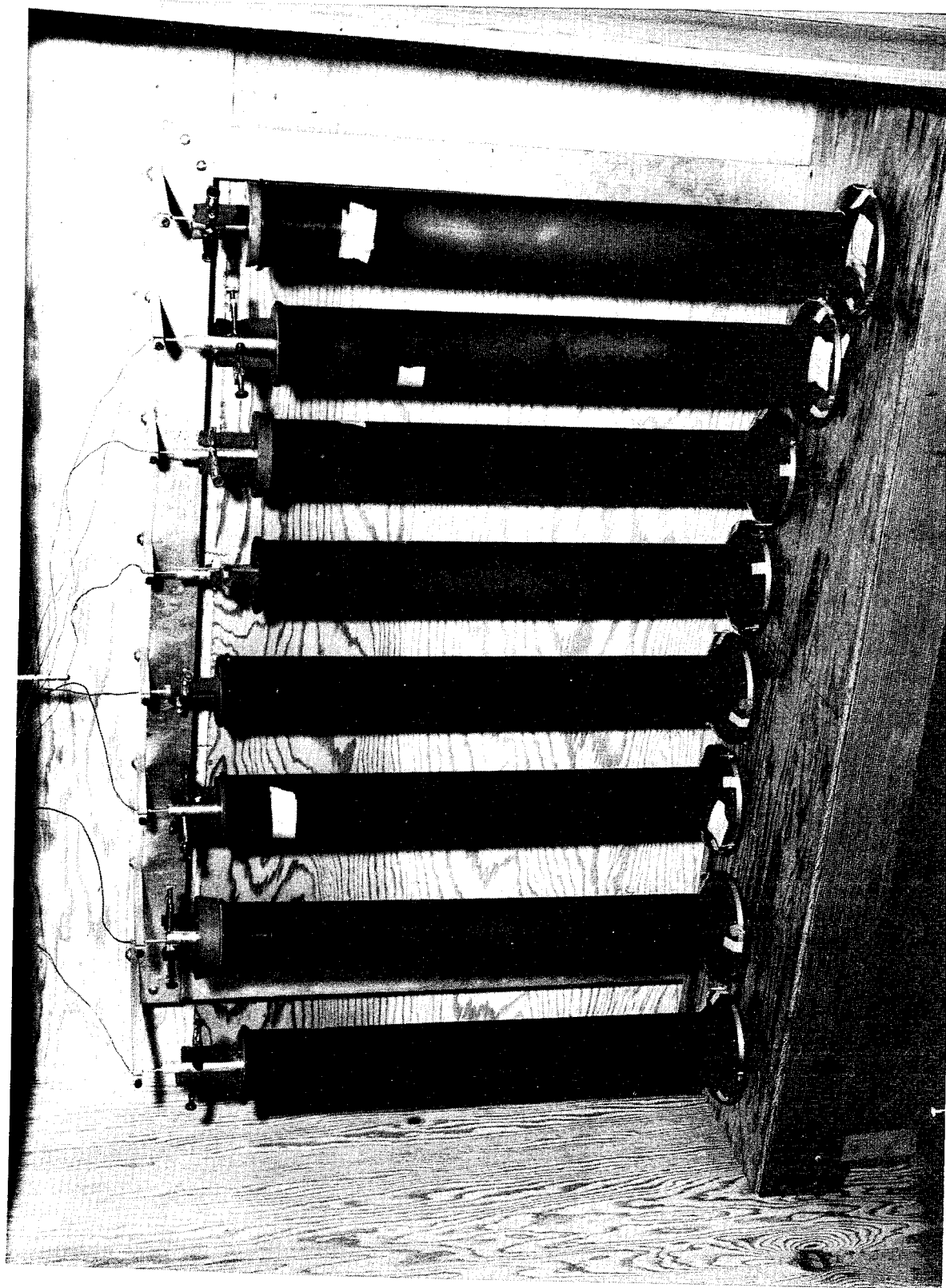


FIGURE 2. IRRADIATION TABLE, TWENTY-FIVE FOOT ROLLS

hydrometer jars. The entire assembly was adjusted, in position or source strength, until it was determined that the incident dose rates were those specified for each of the eight turntable stations, within the error of the dosimetry system. Dosimeters were placed within the cylinders (in air) at the top, middle, and bottom volume occupied by the polyethylene rolls and near the inside surface of the cylinder. The dosimeters were wrapped in lead foil to shield them from low-energy "knockout." The cylinders were rotating in each case so that the measured dose rate was an average of the small difference in rate across the diameter of each cylinder. The target incident dose rate was 20,000 rads per hour. Higher or lower dose rates could then be obtained by decreasing or increasing the source to target distance. Dosimetry at one or two points in the target array would then be sufficient, since the irradiation field was symmetrical and uniform. The results of the dosimetry are shown in Table 1.

C. Procedure for Membrane Evaluation

Candidate membranes were evaluated in a 2" diameter stainless steel reverse osmosis cell similar to that described by Manjikian.⁽¹⁾ A cross section of the cell in use is shown in Figure 3. The presoaked membranes were evaluated at 400 psig pressure with a sodium chloride concentration of 2500 ppm in the feed. Sodium chloride concentrations in feed and product water were determined by electrical conductivity.

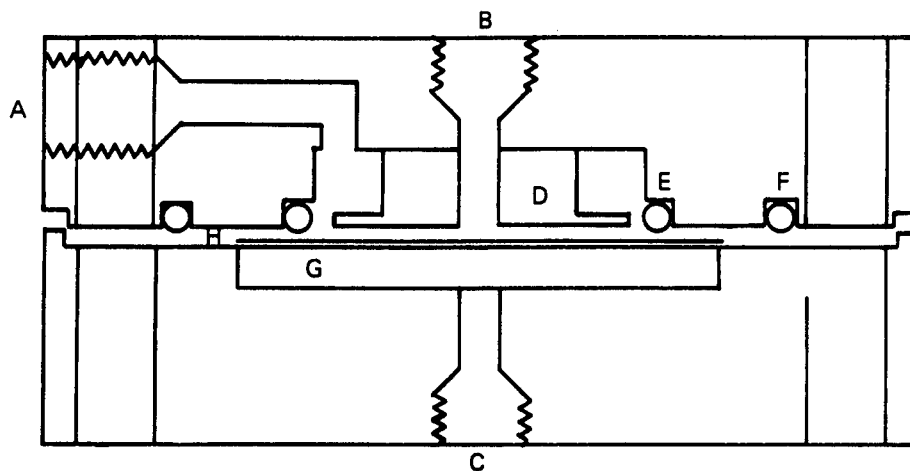
The reverse osmosis test modules were originally designed to avoid the use of pumps. The feed solution was stored in stainless steel tanks which were maintained at the desired operating pressure via compressed air which was fed to the storage tanks by a two-stage pressure regulator, as shown in Figure 4.

The feed flow rate was adjusted by a needle valve at the exit of the cell and was measured on a rotameter. A feed flow rate of about 80 cc per minute was used on the screening runs, which provided a practical run duration per feed tank and did not require excessive refilling of the tanks. Each test module was equipped with two feed tanks and the necessary valves to allow one tank to be refilled while the other was in use, thus allowing long duration runs if desired.

TABLE 1. DOSIMETRY MAPPING OF GAMMA FLUX

Target Trial at 41.0 Inches (full arc)

<u>Position</u>		<u>Dose Rate, Rads x 10⁻⁴ Per Hour</u>
1	Top	2.0
	Center	2.0
	Bottom	2.0
2	Top	2.0
	Center	2.3
	Bottom	2.4
3	Top	2.1
	Center	2.0
	Bottom	2.0
4	Top	2.0
	Center	2.0
	Bottom	2.1
5	Top	2.0
	Center	2.0
	Bottom	2.0
6	Top	2.0
	Center	2.0
	Bottom	2.1
7	Top	2.1
	Center	2.1
	Bottom	2.1
8	Top	2.0
	Center	2.1
	Bottom	2.0



Legend:

- | | |
|--------------------------|---|
| A – Brine Inlet | E – High Pressure O-Ring, 2-Inch Diameter |
| B – Brine Outlet | F – Low Pressure O-Ring |
| C – Product Water Outlet | G – Porous Stainless Steel Plate |
| D – Distribution Plate | H – Membrane Plus Filter Paper Support |

FIGURE 3. REVERSE OSMOSIS CELL

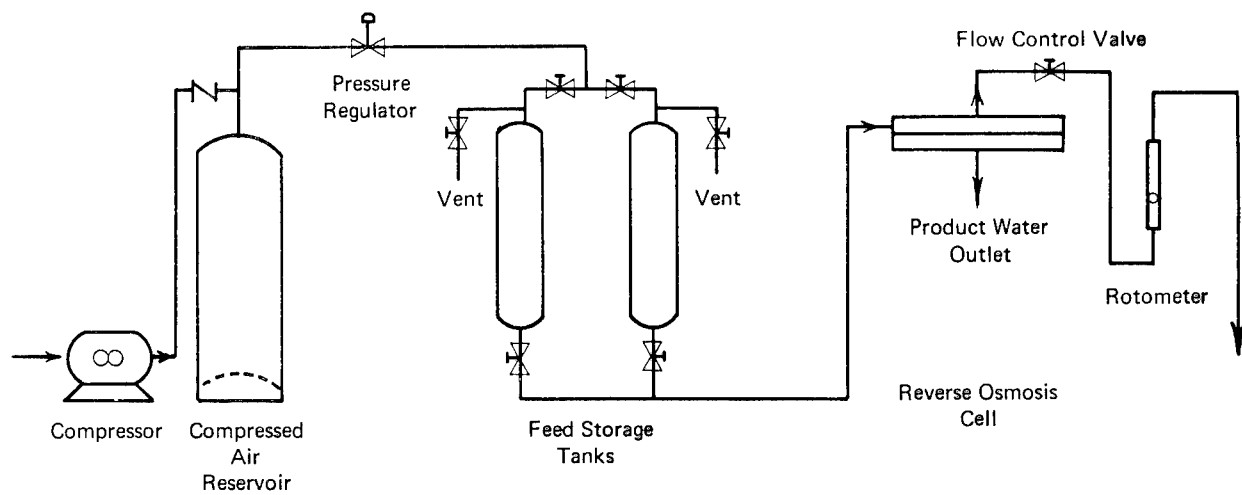


FIGURE 4. REVERSE OSMOSIS TEST MODULE

The reverse osmosis cell is unstirred, as can be seen by Figure 3. The design is such that concentration polarization should be minimized, however. The feed solution enters an annular space and flows across the membrane toward the center of the cell. The flow channel is 20 mils in height, and with a 1-2 mil membrane backed with a 7-8 mil filter paper, the effective flow channel is about 10 mils. While the flow rate is low, and the flow tends to be laminar, the high shear in the flow channel should minimize concentration polarization. To check these reverse osmosis cells, we obtained samples of Eastman's cellulose acetate reverse osmosis membrane. The Eastman membrane RO-97 is claimed to give 96-98% salt rejection with a water flux of 16-22 gfd, when run at 600 psig on 5000 ppm sodium chloride solution. Eastman's literature states that the membrane was evaluated in a 2" diameter cell at a feed flow rate of 800 cc per minute. Results obtained in our test cell at feed flow rates of 23, 78, and 140 cc per minute with 5000 ppm feed at 600 psig are shown in Table 2. As can be seen, the water flux through the membrane was independent of the feed flow rate. However, the salt rejection did increase with increasing feed flow rate, indicative that some concentration polarization does occur with this cell design. At about 80 cc per minute feed rate, the value obtained for the salt rejection was approximately three percent lower than the claimed rejection at a feed rate of 800 cc per minute. It was felt that for screening purposes this discrepancy could be tolerated, since the error due to concentration polarization should be most pronounced with a membrane displaying high flux and high rejection. The observed three percent decrease is probably the maximum error one would obtain with this cell design at a feed flow rate of 80 cc per minute.

During the second quarter of the project, the reverse osmosis module was modified by inclusion of a peristaltic recirculating pump in a pressure housing. The pump housing was constructed so that the internal and external pressure on the pump could be equalized by air pressure, and the pump tubing was exposed only to the pressure drop across the reverse osmosis cells and associated 1/4" tubing. This pumping system was equipped with a variable speed drive and could provide recirculation rates of 600 cc per minute per cell, which corresponds to a feed inlet velocity at the periphery of

TABLE 2. TEST CELL EVALUATION

<u>Feed Flow Rate</u> <u>cc/min</u>	<u>Salt Rejection, *</u> <u>%</u>	<u>Water Flux, *</u> <u>Gfd</u>
23	92.7 \pm 0.2	15.1 \pm 0.1
78	93.4 \pm 0.4	15.2 \pm 0.1
140	93.8 \pm 0.4	15.1 \pm 0.1

* Test Conditions: Eastman RO-97 membrane,
Feed Concentration 5000 ppm NaCl,
Feed Pressure, 600 psig,

the cell of 27 cm/sec, increasing to about 200 cm/sec at the outlet port at the center of the cell.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The initial phase of the experimental work on this program required the preparation of a number of membranes by grafting one-mil polyethylene film with various monomers or monomer mixtures. By then determining the transport properties of the grafted membranes for water and sodium chloride, sufficient understanding of the effect of the modifications of the base polyethylene could be attained to select areas for more intensive studies.

Monomers chosen for modification of polyethylene film included acrylic acid, methacrylic acid, 2-vinylpyridine, hydroxypropyl methacrylate, hydroxyethyl methacrylate, t-butylaminoethyl methacrylate, dimethylaminoethyl methacrylate, and sodium vinylsulfonate. Grafted films using these monomers were successfully prepared except for the case of sodium vinylsulfonate, which did not appear to graft the film. Initially, the films were grafted using a solution containing 25 weight percent monomer. The grafted films were scanned on an infrared spectrometer to ascertain that grafting had occurred.

Some films prepared by grafting are listed in Table 3 with some of their properties. The acid-grafted and base-grafted films are evaluated as their potassium or hydrochloride salts, respectively, since this renders the films more hydrophilic. As can be seen, the wet grafted films are thicker than the one-mil polyethylene starting material. Of the materials shown in Table 3, the acid-grafted films, in the potassium salt form, show the most promise. The vinylpyridine-grafted films as their hydrochloride salts required higher degrees of grafting to give a semipermeable membrane. The films produced by grafting polyethylene with hydroxyalkyl methacrylates (S-18, S-19) and aminoalkyl methacrylates (S-20, S-21) gave negligible water flux when evaluated at 400 psig using 0.25 weight percent aqueous sodium chloride solution.

In Table 4 are listed some films prepared by cograftering polyethylene film, where a mixture of monomers is used, or by re-grafting polyethylene film, where two monomers are grafted onto the film in two sequential grafting operations.

TABLE 3. PREPARATION AND PROPERTIES OF SOME
GRAFTED POLYOLEFIN MEMBRANES

Film No.	Monomer	Grafting Solution, %	Other Components	Grafting Solution, %	Chemical Modification	Wet Thickness, mils	H ₂ O Flux cm/sec x 10 ⁴	Salt Rejection* %
S-12	4-Vinylpyridine	25	--	-	HCl Salt	1.4	Negligible	--
S-13	2-Vinylpyridine	25	--	-	HCl Salt	1.7	Negligible	--
S-16	Methacrylic Acid	25	CCl ₄	5	Potassium Salt	3.2	2.70	52.2
S-18	Hydroxypropyl methacrylate	25	CCl ₄	5	--	1.5	Negligible	--
S-19	Hydroxyethyl methacrylate	25	CCl ₄	5	--	2.3	Negligible	--
S-20	t-Butylaminoethyl methacrylate	25	CCl ₄	5	--	1.3	Negligible	--
S-21	Dimethylaminoethyl methacrylate	25	CCl ₄	5	--	2.3	Negligible	--
S-31	Acrylic Acid	25	K ₃ Fe(CN) ₆	0.3	Potassium Salt	2.8	2.59	53.2
S-37	Acrylic Acid	20	CCl ₄	4	Potassium Salt	1.7	1.35	63.3
S-38	Acrylic Acid	15	CCl ₄	3	Potassium Salt	1.5	1.08	63.4
S-39	Acrylic Acid	10	CCl ₄	2	Potassium Salt	1.2	0.70	68.2
S-40	Acrylic Acid	25	CCl ₄	5	Potassium Salt	1.9	1.64	60.0
S-45	4-Vinylpyridine	50	--	-	HCl Salt	2.4	0.67	67.7
S-46	4-Vinylpyridine	75	--	-	HCl Salt	3.8	1.73	61.2
S-52	Acrylic Acid	25	CCl ₄	5	Potassium Salt	1.9	1.62	58.9
S-53	Acrylic Acid	20	CCl ₄	4	Potassium Salt	1.7	1.28	65.4
S-54	Acrylic Acid	15	CCl ₄	3	Potassium Salt	1.5	1.06	66.8
S-55	Acrylic Acid	10	CCl ₄	2	Potassium Salt	1.5	1.05	67.5

* Test Conditions: 0.25 weight percent NaCl feed solution, 400 psig pressure

TABLE 4. PREPARATION AND PROPERTIES OF SOME
COGRAFTED AND REGRAFTED POLYOLEFIN MEMBRANES

Film No.	Initial Graft		Regraft		Chemical Modification	Wet Thickness, mils	H ₂ O Flux cm/sec x 10 ⁴		Salt Rejection %
	Monomer	Grafting Solution, %	Monomer	Grafting Solution, %			cm/sec x 10 ⁴	Gfd	
S-5	Sodium vinylsulfonate Acrylic Acid	23 10	--	--	Water Washed	1.3	Negligible		--
S-11	4-Vinylpyridine Sodium vinylsulfonate	18 18	--	--	HCl Salt	1.4	Negligible		--
S-24	Sodium vinylsulfonate Acrylic Acid	5 19	--	--	Potassium Salt	3.1	1.91	4.05	59.9
S-6	4-Vinylpyridine Acrylic Acid	20 5	--	--	HCl Salt Free Acid	1.6	Negligible		
S-29	4-Vinylpyridine Acrylic Acid	5 20	--	--	Potassium Salt	2.8	2.12	4.49	57.3
S-9	4-Vinylpyridine	25	Acrylic Acid	25	Potassium Salt	3.1	2.80	5.94	48.5
S-15	4-Vinylpyridine	25	N-Vinyl-2-pyrrolidone	20	HCl Salt	2.4	1.00	2.12	66.1
S-23	2-Vinylpyridine	25	Acrylic Acid	25	Potassium Salt	5.1	0.86	1.82	65.8
S-25	4-Vinylpyridine	25	Acrylic Acid	15	Potassium Salt	5.8	1.73	3.67	55.1
S-26	2-Vinylpyridine	25	Acrylic Acid	15	Potassium Salt	5.8	1.08	2.29	61.5
S-29X	4-Vinylpyridine Acrylic Acid	5 20	Divinylbenzene	1	Potassium Salt	2.5	1.24	2.63	67.2
S-30	2-Vinylpyridine Acrylic Acid	5 20	Divinylbenzene	1	Potassium Salt	2.8	3.66	7.76	68.1
S-44	Acrylic Acid	25	Vinyl Acetate	25	Potassium Salt	3.3	2.41	5.11	55.1

* Test Conditions: 0.25 weight percent NaCl feed solution, 400 psig pressure.

Cografting was employed with sodium vinylsulfonate using acrylic acid or 4-vinylpyridine as comonomer. The vinylpyridine-sodium vinylsulfonate film (S-11) had negligible water flux, as did an acrylic acid-sodium vinylsulfonate film (S-5) with low acrylic acid content (10 weight percent) in the grafting solution. However, when the grafting solution consisted of 19 percent acrylic acid and 5 percent sodium vinylsulfonate, a film (S-24) was produced which gave a water flux of 4.05 gfd with 60 percent salt rejection, while a film (S-37, Table 3) grafted with 20 percent acrylic acid alone had a water flux of 2.85 gfd and a salt rejection of 63 percent. The cografted film had a thickness of 3.1 mils compared to 1.7 mil for the acrylic acid-grafted film. As can be seen in Table 4, cografting or regrafting of vinylpyridine films with acrylic acid or N-vinyl-2-pyrrolidone to enhance the hydrophilicity produced films which behaved as semi-permeable membranes, while the straight vinylpyridine grafted films at the same level of grafting did not. That the techniques of cografting and regrafting can be combined is shown in two films (S-29X and S-30) in Table 4. These cografted acrylic acid-vinylpyridine films were regrafted with divinylbenzene to crosslink the membranes and give a tighter membrane structure. That this was accomplished can be seen by comparing film S-29X with film S-29. The cross-linked film has lower water flux and higher salt rejection, indicative of a tighter membrane structure. As evidenced by the variations in the properties of the cografted and regrafted films in Table 4, there are modifications in the structure of the film which can be accomplished by these procedures.

In the early stages of the program, an attempt was made to determine the phenomenological coefficients of hydraulic permeability L_p , salt permeability ω , and reflection σ , as derived by Spiegler and Kedem.⁽²⁾ However, it was found that the hydraulic permeability L_p decreased as the applied pressure to the reverse osmosis cell was increased when using deionized water as feed, as shown in Table 5. This decrease in L_p with increasing pressure appears to be inherent in the grafted films. As can be seen, the water flux increased only 16 percent with a 4-vinylpyridine-acrylic acid film (S-9) and increased only 27 percent with a methacrylic acid film (S-16) when the feed pressure was increased from 400 to 800 psi, instead of doubling as would be expected if L_p were a constant. It is

TABLE 5. THE EFFECT OF PRESSURE ON THE HYDRAULIC PERMEABILITY OF GRAFTED POLYOLEFIN MEMBRANES

P, atm	Membrane Number			
	S-9		S-16	
	Flux, $J_v \times 10^4$ cm/sec	$L_p \times 10^5$ J_v/P	Flux, $J_v \times 10^4$ cm/sec	$L_p \times 10^5$ J_v/P
27.2	4.39	1.61	2.99	1.10
40.8	4.87	1.19	3.72	0.91
54.4	5.10	0.94	3.81	0.70

believed that this behavior is due to the nature of the interaction of these grafted films with water. These films are hydrophilic and swell rapidly and reversibly when placed in water. It appears that when pressure is applied to a wet, swollen membrane, a portion of the imbibed water is forced out of the membrane with a resultant decrease in the volume. Since a grafted membrane under hydraulic pressure does not contain as great a volume of imbibed water as an unrestricted membrane, the membrane structure is tighter, and the permeation rates through the membrane are lower. However, the volume change of the grafted membranes is reversible, in that the membrane upon release of the pressure will reimbibe water and swell to its original volume. Thus, the degree of hydration of these grafted membranes, and hence the membrane structure, are functions of the hydraulic pressure applied across the membrane. This precludes the determination of meaningful phenomenological coefficients as defined. (2)

Efforts were made to determine the degree of grafting of acrylic acid-modified polyethylene films. A qualitative measurement of grafting can be obtained by infrared spectroscopy. Neutralization of acid-grafted films with potassium hydroxide and determination of the chemically bound potassium was tried as a quantitative measure of grafting, but the results obtained were not reproducible.

Two series of films were produced in which the acrylic acid concentration in the grafting solution was varied from 10 to 25 weight percent. In both series, the weight ratio of acrylic acid to carbon tetrachloride (used as a chain transfer agent) was maintained constant. Infrared spectroscopy indicated that the concentration of the acrylic acid in the grafted film increased with increasing acrylic acid concentration in the grafting solution. The effect of increasing acrylic acid concentration in the grafting solution on water flux and salt rejection is shown in Figures 5 and 6, respectively, for both series of membranes. As the acrylic acid concentration in the grafting solution and hence in the membrane increased, the water flux increased and the salt rejection decreased, as measured at 400 psig with 0.25 weight percent sodium chloride feed. The numerical values for flux and salt rejection agree well for given acrylic acid concentrations, except for the films grafted with 10 weight percent

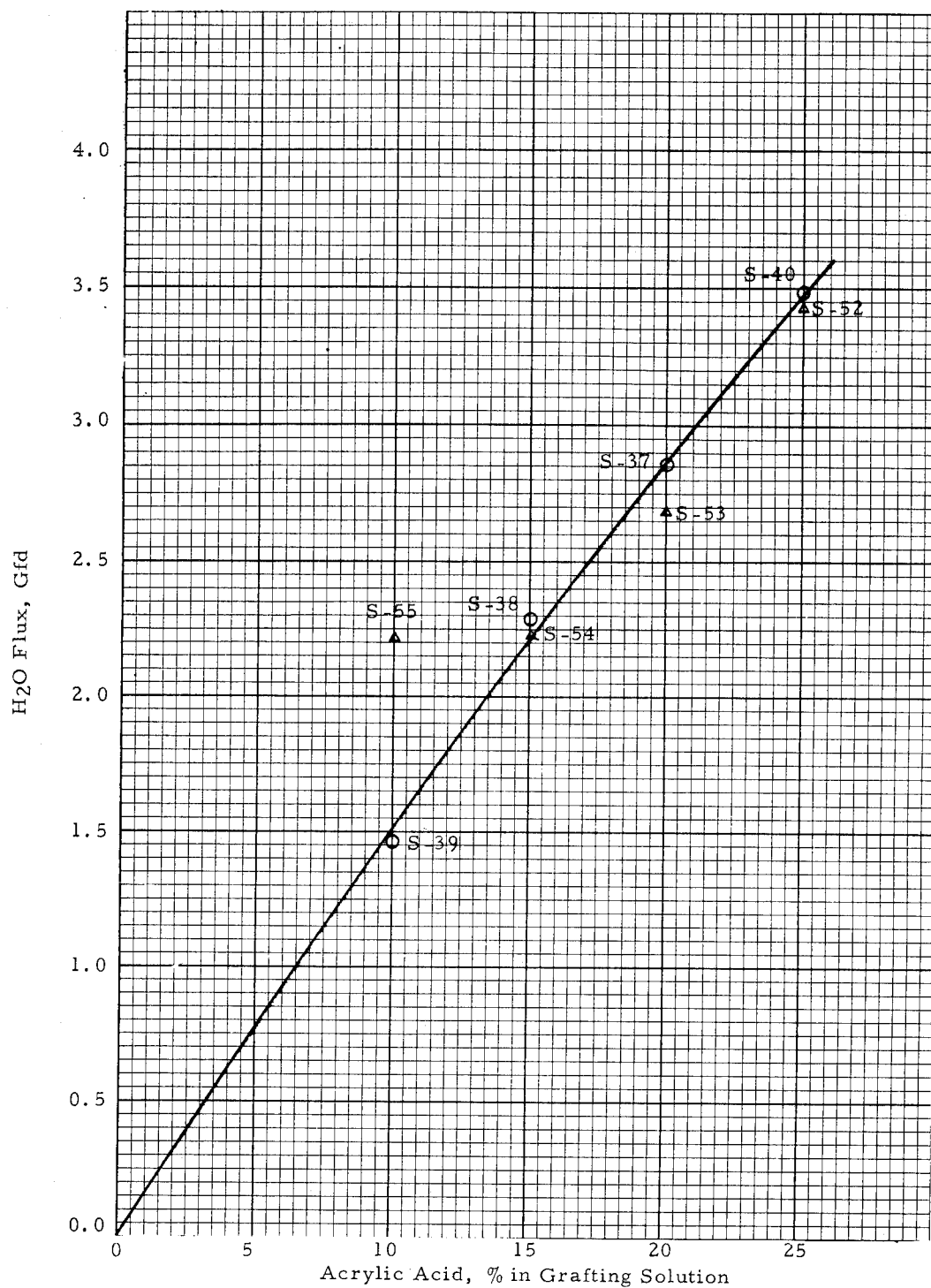


FIGURE 5. THE EFFECT OF ACRYLIC ACID CONCENTRATION ON WATER FLUX

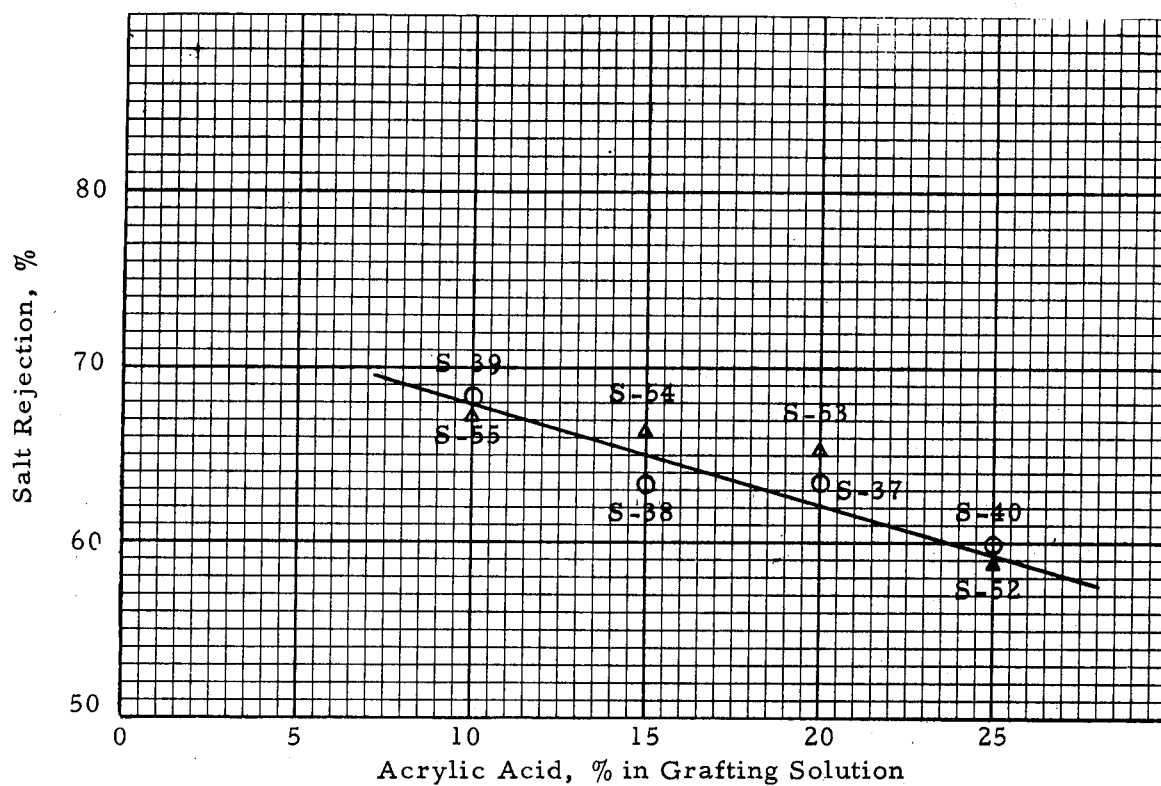


FIGURE 6. THE EFFECT OF ACRYLIC ACID CONCENTRATION IN THE GRAFTING SOLUTION ON SALT REJECTION

acrylic acid, where film S-55 shows an appreciably high water flux compared to that of film S-39. However, the salt rejections for these two films are similar. No explanation for the relatively high water flux for film S-55 can be offered at this time. The only difference in the two series of films is in the polyethylene base stock used. The base stock in both cases is one-mil film, but there are differences in average molecular weight and molecular weight distribution. These differences in polyethylene base stock do not normally appear to affect the transport properties of the grafted film but may affect the physical properties such as tensile strength and elongation. It should be mentioned that all the polyethylene film used in these studies is a special additive-free grade of material. Additives normally used as antioxidants, antistatic agents, slip agents and the like can result in irregular or ineffective grafting, since many of the materials used for these purposes can function as radical scavengers and so behave as chain terminators.

A series of runs was made using cheesecloth as a backing material and using acrylic acid concentrations of 10, 15, 20 and 25 wt % in the grafting solution to determine the degree and uniformity of grafting obtained. The ratio of acrylic acid to chain transfer agent (CCl_4) was maintained constant at 5 to 1. During the process of rolling the twenty-five foot rolls of polyethylene, a small section of the film was cut from the roll, at five-foot intervals, weighed and the weight recorded, and replaced in the roll. The rolls were placed in the hydrometer jars, filled with the desired grafting solution in the usual manner, and irradiated. The grafted material was washed free of homopolymer in five-percent caustic and air dried. The weighed samples were converted back to the free acid form and dried to constant weight in a vacuum desiccator. From the weight increase in these samples, the degree of grafting and the weight percent polyacrylic acid in the graft copolymer were calculated. Comparison of these values for each set of samples gave an indication of the uniformity of the graft throughout each twenty-five foot roll. The data obtained in this study are given in Table 6.

As can be seen, the material produced at each concentration of acrylic acid is quite uniform. Also, as shown in Figure 7, the degree of grafting, which is a measure of the amount of poly(acrylic

TABLE 6. THE EFFECT OF ACRYLIC ACID CONCENTRATION IN THE GRAFTING SOLUTION ON THE COMPOSITION OF THE GRAFT COPOLYMER

Film No.	Grafting Solution Composition, wt %			Sample Distance from End of Roll, ft	Degree of Grafting*	Polyacrylic Acid in Product, wt %	Polyacrylic Acid, meq/gram Copolymer
	Acrylic Acid	CCl ₄	C ₆ H ₆				
S-81	25	5	70	5	0.85	45.6	6.25
				10	0.86	46.2	6.32
				15	0.89	47.2	6.46
				20	0.86	46.4	6.36
S-82	20	4	76	5	0.75	42.9	5.88
				10	0.69	40.9	5.60
				15	0.64	39.1	5.36
				20	0.71	41.7	5.71
S-83	15	3	82	5	0.51	33.9	4.64
				10	0.50	33.1	4.53
				15	0.51	33.7	4.61
				20	0.54	34.9	4.78
S-84	10	2	88	5	0.40	28.6	3.92
				10	0.37	27.0	3.70
				15	0.37	27.1	3.71
				20	0.38	27.4	3.75

* Weight of polyacrylic acid in the graft copolymer/weight of starting polyethylene.

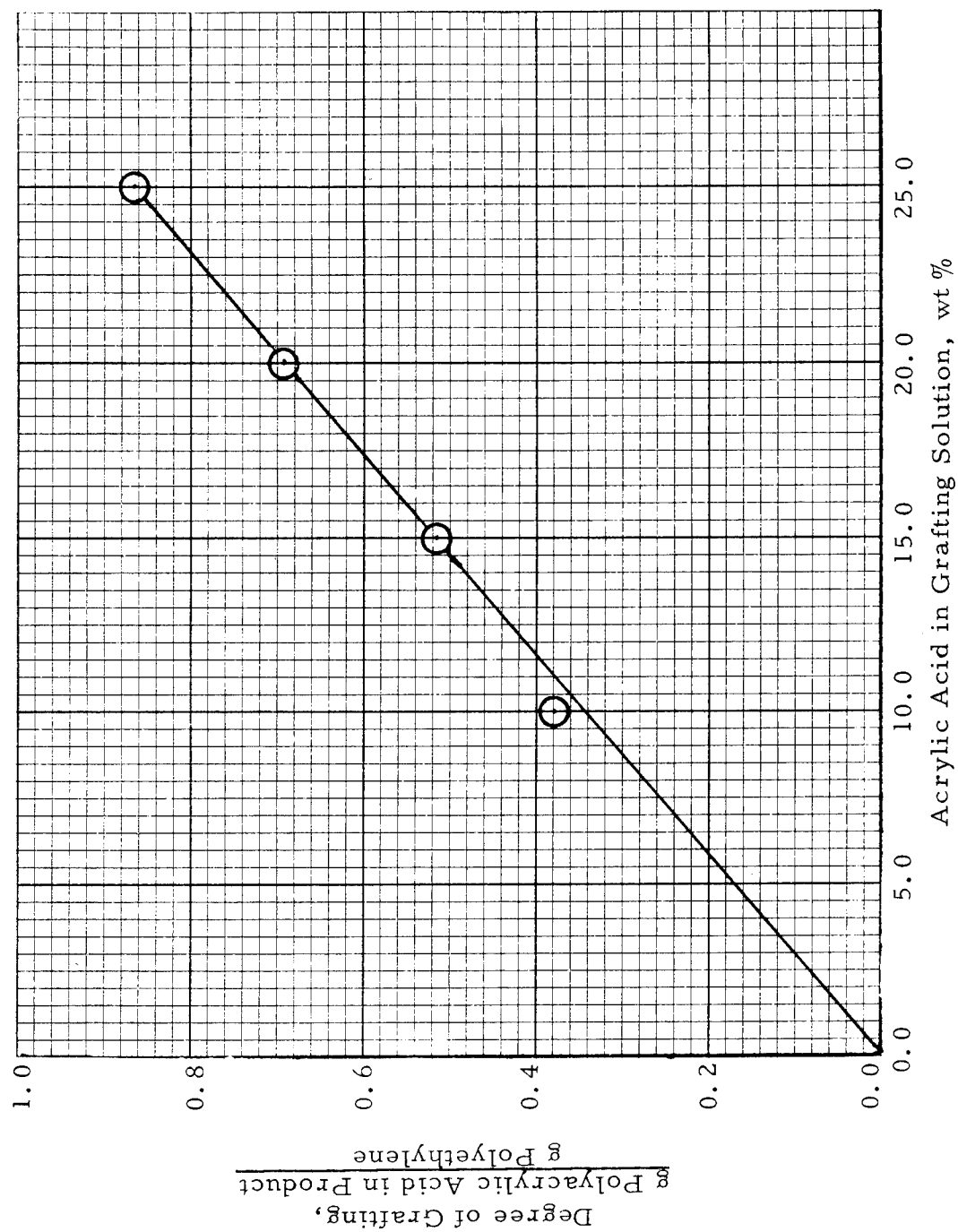


FIGURE 7. THE EFFECT OF ACRYLIC ACID CONCENTRATION IN THE GRAFTING SOLUTION ON THE DEGREE OF GRAFTING OF POLYETHYLENE FILM

acid) formed per unit weight of starting polyethylene, is a linear function of the acrylic acid concentration in the grafting solution. Since the poly(acrylic acid) content of these films was known, equilibrium water content, water flux, salt rejection, and the membrane constant A were determined. The data are presented in Table 7.

The equilibrium water concentration for these films was obtained by soaking portions of film in the potassium salt form for 24 hours in deionized water, blotting the surface, and weighing in tared weighing vials. The films were dried to constant weight in the vials in a 110°C circulating air oven and reweighed to determine the water content by weight loss and to obtain the dry weight of the films. As can be seen from the data presented in Table 7 and in Figure 8, the equilibrium water concentration of acrylic acid-grafted films in the potassium salt form is a linear function of the amount of potassium polyacrylate in the membrane.

The water flux and salt rejection for these membranes were determined at 400 psig with 0.25 wt % saline feed. As the amount of potassium polyacrylate in the film decreased, the water flux decreased, and the salt rejection increased. Examination of the data presented in Table 7 suggested that the decreasing flux observed with decreasing potassium polyacrylate content might be explained by the decreasing equilibrium water concentration in the graft copolymer. As shown in Figure 9, when the membrane constant A is plotted as a function of the equilibrium water concentration of the films, a good straight line fit is obtained. If this is accepted to mean that water transport through potassium polyacrylate-grafted membranes is a direct function of the amount of imbibed water in the membrane, and the demonstrated facts of strongly coupled water-salt flows along with very high equilibrium water contents are considered, then the following mechanism of transport through these membranes can be proposed.

In the wet state, the films contain large amounts of imbibed water and are in a swollen, gel-like state. The water in interstitial spaces between the polymer chains provides a medium for ionization of the potassium polyacrylate, which results in mobile potassium ions in the interstitial spaces and fixed carboxyl ions on the polymer chains.

TABLE 7. THE EFFECT OF POLY(ACRYLIC ACID) CONTENT OF
THE GRAFT COPOLYMER ON FILM PROPERTIES

Film No.	Acrylic Acid Content - wt % in Copolymer	Equilibrium Water Content ¹ wt %	Water Flux ² Gfd	Salt Rejection %	Membrane Constant A cm ³ /cm ² /sec/Atm x 10 ⁵
S-81	46.4	185	2.84	67.7	0.49
S-82	41.2	179	2.78	68.9	0.48
S-83	33.9	150	2.48	69.0	0.43
S-84	27.5	126	2.27	72.2	0.39

¹ $\frac{\text{Weight wet} - \text{weight dry}}{\text{weight dry}}$, film as potassium salt

² Film as potassium salt, 0.25 wt % saline feed, 400 psig.

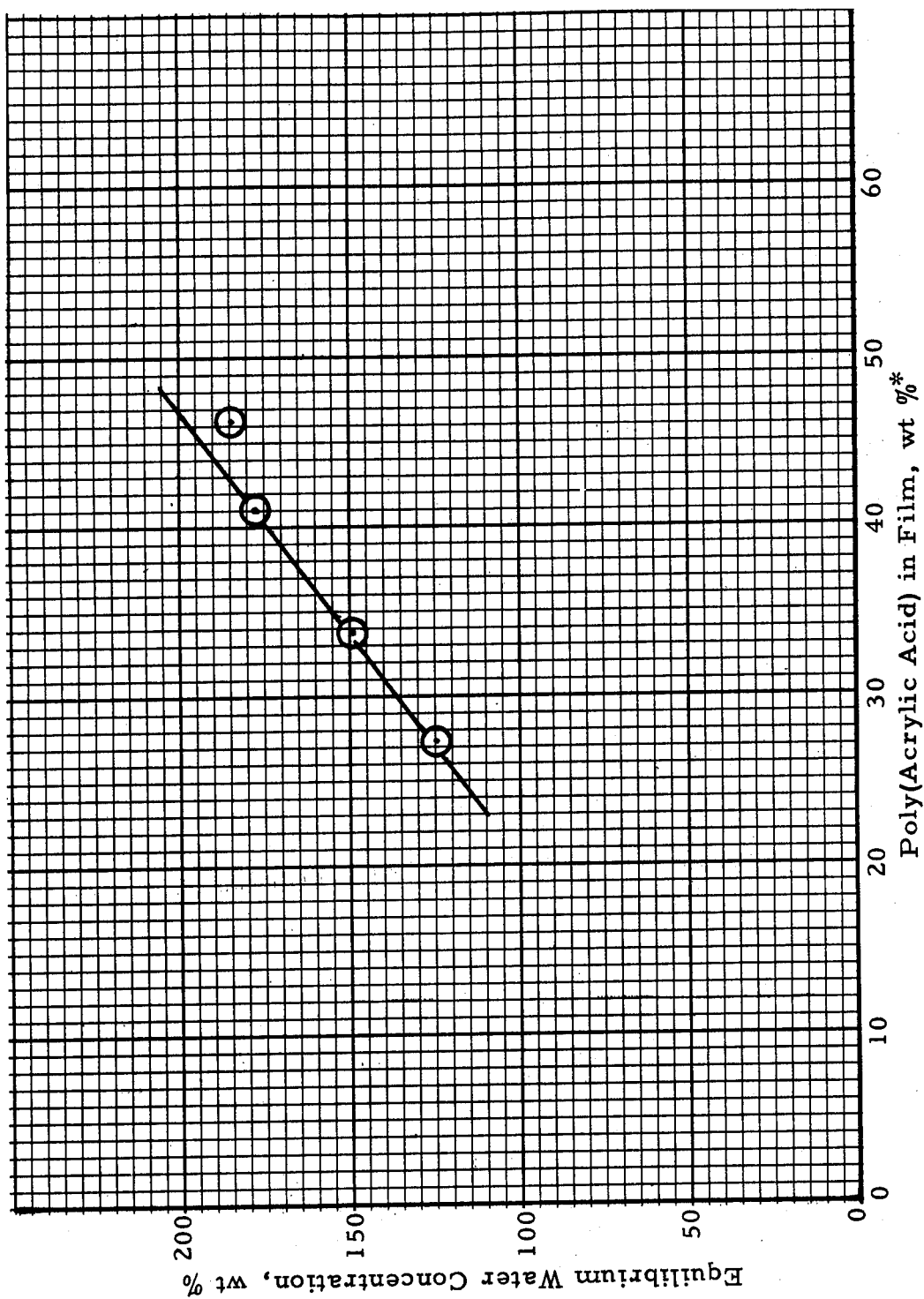


FIGURE 8. THE EFFECT OF POLY(ACRYLIC ACID) CONTENT IN THE FILM ON WATER ABSORPTION

* Potassium Salt Form

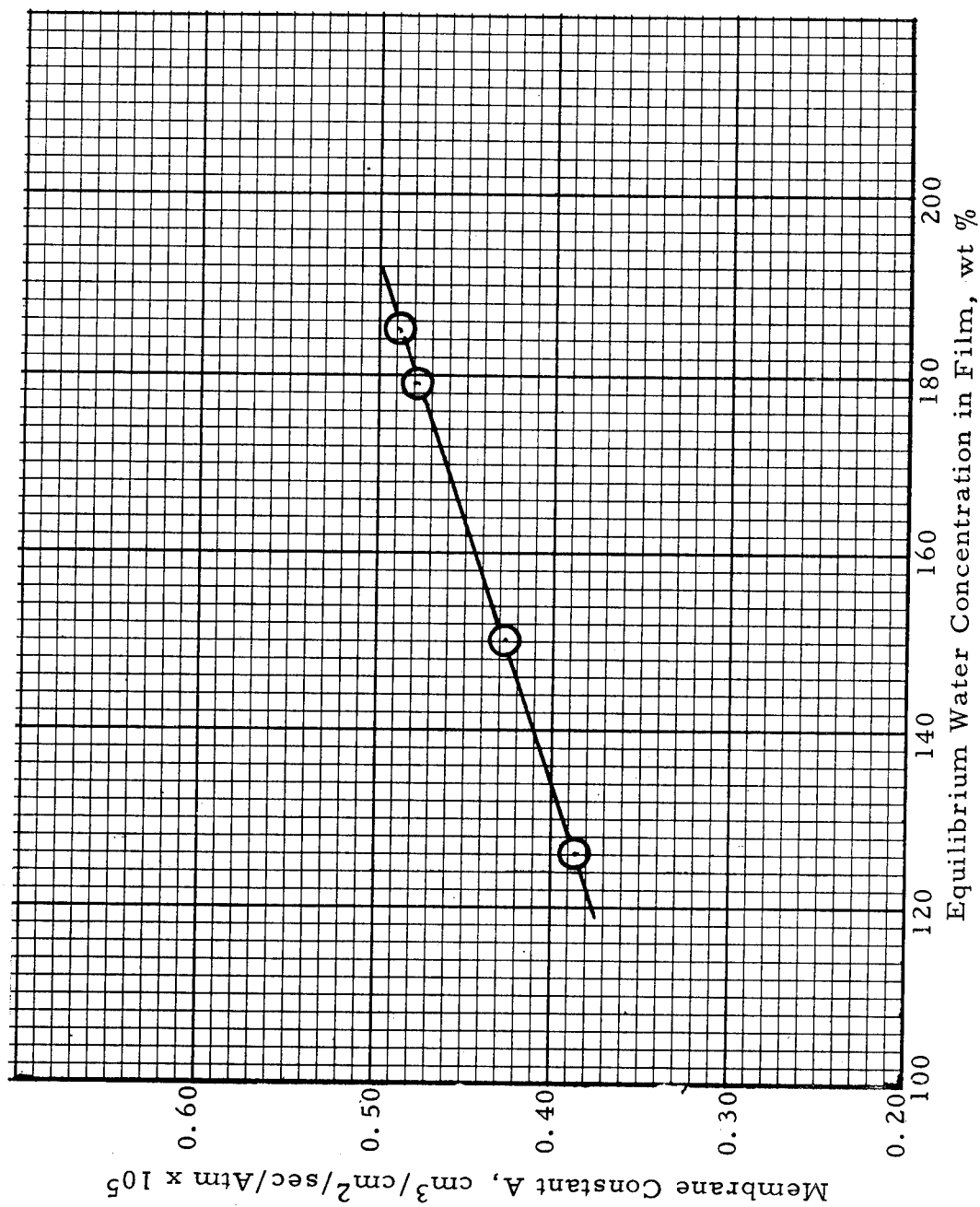


FIGURE 9. THE EFFECT OF ABSORBED WATER CONTENT IN
ACRYLIC ACID GRAFTED FILMS ON WATER TRANSPORT

Water transport through the membrane under hydraulic pressure would occur by viscous flow through the interstitial spaces and would increase with increasing degree of hydration, since the cross-sectional area between the polymer chains would increase as the polymer chains were forced farther apart by the larger volume of imbibed water. Salt rejection in the solution moving through the interstitial space would be due to simple ion exclusion and would decrease as the degree of hydration increases, since the average charge density in the interstitial spaces due to the fixed carboxyl ions on the polymer chains would decrease as the polymer chains occupy a decreasing percent of the hydrated volume of the swollen film. Where the salt rejection is due to ion exclusion, divalent cations should be more selectively rejected than monovalent cations due to their larger diameter and greater charge density.

Reverse osmosis runs utilizing 0.028 molar sodium sulfate and 0.028 molar dibasic sodium phosphate were conducted. It was assumed that, with larger polyvalent anions, the effective repulsion due to the fixed negative charge on the polymer carboxyl groups would be greater, and higher rejections of these salts would be obtained. As can be seen from the data shown in Table 8, rejections of 90% or better were obtained in both cases, using four different films with varying amounts of poly(acrylic acid) in the film. With sodium sulfate, the rejection was essentially constant at 91%, while water flux appeared to decrease with decreasing degree of grafting except for Sample S-82, which has a slightly higher flux than S-81. This decrease in water flux parallels that observed in reverse osmosis experiments on this series of films with sodium chloride. However, the water fluxes were slightly higher with the sodium sulfate feed, compared to sodium chloride feed.

When dibasic sodium phosphate was utilized as feed, salt rejections were 90% or better, and water fluxes were comparable to those obtained with the other solutes. With the phosphate feed, a trend of decreasing flux and increasing rejection with decreasing degree of grafting is seen, except for Sample S-83, which shows a higher than expected flux with a lower rejection.

TABLE 8. REJECTION OF VARIOUS SOLUTES BY ACRYLIC ACID
GRAFTED POLYETHYLENE MEMBRANES

Membrane No.	Na Cl 0.046 M			Na ₂ SO ₄ 0.028 M			Na ₂ H PO ₄ 0.028 M			Poly(acrylic acid) Content, wt % in Copolymer
	Flux Gfd	S. R. %	Membrane Constant A*	Flux Gfd	S. R. %	Membrane Constant A*	Flux Gfd	S. R. %	Membrane Constant A*	
S-81	2.84	67.7	0.49	2.98	91.5	0.52	2.86	91.2	0.50	46.4
S-82	2.78	68.9	0.48	3.02	90.9	0.53	2.54	91.8	0.45	41.2
S-83	2.48	69.0	0.43	2.72	90.8	0.47	3.24	90.0	0.57	33.9
S-84	2.27	72.2	0.39	2.43	91.0	0.42	1.54	93.0	0.27	27.5

* cm³/cm² Sec Atm x 10⁵

All data obtained at 400 psig.

These results seem to bear out the postulate that rejection by these membranes is due to ion exclusion and would seem to indicate that increasing the charge density on the membrane, either through grafting with such monomers as sodium styrene sulfonate or by reducing the degree of hydration of the carboxylic acid-grafted films, would lead to improved rejections.

A series of grafted films was prepared in which the concentration of acrylic acid in the grafting solution was held constant at 25 wt % and the concentration of chain transfer agent, in this case carbon tetrachloride, was varied from zero to 12 wt % in two percent increments. Irradiation dose rate was the same in all cases to give a constant initiation rate within the films. Since the rate of grafting and the rate of chain transfer are dependent upon the rate of diffusion of monomer and chain transfer agent into the film, the rate of grafting should be approximately the same in all runs, and the rate of chain transfer should increase as the concentration of chain transfer agent increases. The net result should be grafted films with the same nominal degree of grafting but with decreasing average molecular weights of the acrylic acid side chains as the concentration of chain transfer agent increases.

The data obtained on evaluating this series of films are given in Table 9. As can be seen, there is no trend evident in either the membrane constant, the water flux, or the salt rejection. These data appear to indicate that at a given degree of grafting, there is no significant effect of the length of the poly(acrylic acid) side chains on the transport properties of the grafted films but that the transport properties depend only on the degree of grafting.

Since the acid-grafted membranes in the potassium salt form are hydrophilic and swell considerably when placed in water, it was decided to prepare a membrane using a divalent cation in order to provide some ionic crosslinking between carboxyl groups. It was reasoned that this might provide a tighter membrane structure and lead to higher salt rejection. Since some loss of flux was anticipated, a membrane (S-63) with a relatively high flux of 5.6 gfd and a salt rejection of 59.9 percent was chosen. The membrane in the potassium salt form was converted to the cupric salt or to a 25 mole

TABLE 9. THE EFFECT OF CHAIN TRANSFER AGENT
CONCENTRATION ON GRAFTED POLYETHYLENE FILM

Film No.	Terminator Concentration (%)	Flux* Gfd	Salt Rejection (%)	Membrane Constant A $\text{cm}^3/\text{cm}^2/\text{sec}/\text{Atm} \times 10^5$
S-56	0	3.43	65.2	0.59
S-57	2	3.02	67.3	0.53
S-58	4	3.20	64.8	0.56
S-59	6	2.79	65.7	0.48
S-60	8	4.54	59.0	0.78
S-61	10	2.91	64.5	*0.50
S-62	12	3.43	64.1	0.59

* Conditions: All films as potassium salt; feed, 0.25% saline;
400 psig.

percent, a 50 mole percent, or a 75 mole percent cupric salt by ion exchange with cupric sulfate solutions of suitable concentration. The cupric and mixed potassium-cupric methacrylate membranes were evaluated, with the results obtained shown in Table 10.

With 25 percent of the potassium exchanged for copper, a doubling of the flux was obtained with a loss of salt rejection of 25 percent. Inclusion of 50 percent, 75 percent, or 100 percent copper in the membrane led to flux values as high as 65.7 gfd with salt rejection as low as 8.4 percent. The flux of the present samples does not correlate with the amount of copper in the film, but due to the manner in which the films were prepared, the exact ratio of copper to potassium in the mixed salt films is not known. That the changes which occurred on formation of the copper salts were reversible was demonstrated by washing the membrane free of copper with a dilute hydrochloric acid solution and converting the resulting acid membrane to the potassium salt form with 5 wt % aqueous potassium hydroxide. These membranes displayed flux and salt rejection essentially identical with that given in Table 10 for the membrane in the potassium salt form.

The effect of thermal treatment of grafted films was also investigated. Two approaches were initially used. One involved heating the films in a circulating air oven at 106°C for one hour. The second involved heating the film in deionized water in a glass pressure bottle for four hours at 106°C. The four films used (S-52, S-53, S-54, S-55) were grafted, respectively, with solutions containing 25, 20, 15, and 10 wt % acrylic acid in benzene. All films were in the potassium salt form and were evaluated at 400 psig with 0.25 wt % saline. The data obtained are shown in Table 11. Standard films, prepared in the usual manner but not heat-treated, are shown for comparison.

Heating in air drastically reduced the flux of the films. The flux on two films was too low to obtain an accurate measurement. As would be expected, the reduction in flux was accompanied by an increase in salt rejection.

TABLE 10. A COMPARISON OF THE POTASSIUM, COPPER, AND MIXED POTASSIUM-COPPER SALTS OF METHACRYLIC ACID-GRAFTED POLYETHYLENE FILM

Film Composition		Flux, Gfd	S. R. %	Membrane Constant A $\text{cm}^3/\text{cm}^2/\text{sec}/\text{Atm} \times 10^5$
% Carboxyl As Cu^{++} Salt	% Carboxyl As K^+ Salt			
100	--	50.2	8.4	8.78
75	25	33.3	18.3	5.78
50	50	65.7	8.4	11.40
25	75	11.9	44.8	2.05
--	100	5.6	59.9	1.04

Membrane S-63, grafted with 25 wt % methacrylic acid solution, copper salts formed by ion exchange with the potassium salt form.
Test conditions -- 400 psig, 0.25 wt % saline.

TABLE 11. THE EFFECT OF HEAT TREATING
GRAFTED POLYETHYLENE FILMS

Film No.	Standard		Heated in Air		Heated in Water	
	Flux Gfd	S. R. %	Flux Gfd	S. R. %	Flux Gfd	S. R. %
S-52	3.44	58.9	1.68	71.8	14.03	38.1
S-53	2.68	65.4	1.19	69.4	14.70	37.5
S-54	2.24	66.8	very slow	----	13.10	39.1
S-55	2.22	67.5	very slow	----	13.14	40.9

In view of the rather large increase in flux by a factor of 4 to 6, the wet thermal treatment of acrylic acid grafted films was further investigated to determine the effect of the time of heating.

When samples of a membrane were heated for periods of up to five hours at 115°C, it was found that the maximum effects of heating were obtained in two hours, and no further changes in flux or salt rejection were observed on continued heating, as is evident from the data presented in Table 12. It was noted that while the transport properties of the film did not change on heating beyond two hours, the material suffered a continuing loss of strength. The films heated for 4 and 5 hours were very tender and required careful handling. This loss of strength implied that changes in the structure of the copolymer had occurred. That irreversible changes in structure had occurred was demonstrated by drying a portion of a heat-treated membrane which had shown a flux after heat treating at 106°C of 14.7 gfd with a salt rejection of 37.5 percent, compared to 2.68 gfd and 65.4% salt rejection prior to heat treatment. The membrane was air dried for 48 hours at ambient temperature and subsequently rehydrated by soaking overnight in deionized water. The membrane after this treatment had a flux of 13.8 gfd and a salt rejection of 37.9 percent.

Heating acrylic acid-grafted membranes in water appears to lead to changes in the structure of the polymer with a resultant increase in flux, a decrease in the salt rejection, and a loss of mechanical strength. Since the heat-treated membranes were less strong, the effect of operating pressure on membrane performance was investigated. The flux, salt rejection, and membrane constant A were determined at four pressures, with 0.25 wt % saline feed for a heat-treated membrane, and compared with similar data for a non-heat-treated membrane. Results are shown in Table 13. A comparison of the membrane constants shows that in both cases there was a decrease in the membrane constant of about 50% on going from 27 to 68 atmospheres. However, for the heat-treated membrane, the salt rejection remained essentially constant, while for the non-heat-treated membrane the salt rejection increased 22% over this pressure range. In view of the apparent changes in membrane structure on heating in air and water, a final study to determine the effect of thermal treatment in various media on the transport properties of acrylic

TABLE 12. HEAT TREATING GRAFTED POLYETHYLENE FILM --
THE EFFECT OF TIME OF HEATING IN WATER

<u>Time (hrs)</u>	<u>Flux, Gfd</u>	<u>S. R. %</u>	<u>Membrane Constant A cm³/cm²/sec/Atm x 10⁵</u>
0	5.49	53.2	0.95
1	8.64	38.3	1.50
2	13.21	36.1	2.29
3	13.33	32.7	2.31
4	15.35	35.2	2.66
5	13.02	32.7	2.25

Membrane S-31, grafted with 25 wt % acrylic acid solution, potassium salt form, heated in H₂O at 115°C. Test conditions -- 400 psig, 0.25 wt % saline feed.

TABLE 13. HEAT-TREATED AND STANDARD GRAFTED
POLYETHYLENE MEMBRANES AT VARIOUS
OPERATING PRESSURES

P Atm.	Membrane Number					
	S-31-HW2*			S-44		
	Flux, Gfd	S. R. %	Membrane Constant A $\text{cm}^3/\text{cm}^2/\text{sec}/\text{Atm} \times 10^5$	Flux, Gfd	S. R. %	Membrane Constant A $\text{cm}^3/\text{cm}^2/\text{sec}/\text{Atm} \times 10^5$
27.2	12.1	33.2	2.11	5.8	46.4	1.00
40.8	13.3	33.5	1.53	6.7	51.6	0.77
54.4	13.8	34.4	1.20	7.0	54.0	0.61
68.0	14.1	34.4	0.98	7.1	56.7	0.50

Feed - 0.25% saline

* Heat treated at 115°C for two hours in H₂O

acid-grafted polyethylene film was made. A film (S-81) grafted with 25 wt % acrylic acid in the grafting solution and containing 46.4 wt % poly(acrylic acid) was chosen for the study. This film was used in the form of the potassium salt, and all evaluations on the heat-treated films were carried out using 0.25 wt % saline at 400 psig.

The thermal treatment was conducted by heating samples in air, in water, or in toluene at the desired temperature for a specified time. Heating in water at 108°C was accomplished in a small stainless steel pressure vessel. Heating in air at 108°C was in a circulating air oven, and heating in toluene was accomplished at the boiling point of the solvent (110°C). The results obtained are shown in Table 14.

As previously found, heating in air led to a reduction in flux with a small increase in salt rejection, as compared to a standard sample. Heating in water produced a large increase in flux, but with a loss of salt rejection, while heating in toluene led to a small loss of flux with essentially no change in salt rejection. Heat treating in two different media in sequential steps, for example heating in air followed by heating in water or toluene, led to results similar to heating in the second medium alone, indicating that the morphology of the film is a direct result of its most recent environment.

In an attempt to limit the degree of swelling of acrylic acid-grafted membranes and possibly improve their salt rejecting properties, grafted films were prepared utilizing a mixture of acrylic acid and either vinyl acetate or acrylonitrile in various weight ratios. It was thought that by cografting a relatively hydrophobic material along with acrylic acid, a graft terpolymer might be prepared in which the side chains on the polyethylene base stock would consist of a random distribution of hydrophobic and hydrophilic segments. This could result in a structure in which water could diffuse but which would not swell to as great an extent as a film grafted with acrylic acid alone. As shown in Table 15, two series of films were prepared, maintaining the total monomer concentration in the grafting solution at 25 wt % and varying the weight ratio of acrylic acid to comonomer from 0.25 to 4.

TABLE 14. THE EFFECT OF HEAT TREATMENT IN VARIOUS MEDIA
ON THE TRANSPORT PROPERTIES OF ACRYLIC ACID-
GRAFTED POLYETHYLENE FILMS

Membrane No.	Thermal Treatment				S. R. %	Membrane Constant $A \times 10^5$ cc/cm ² sec Atm
	Media	Temp °C	Time hrs.	Flux Gfd		
S-81	--	--	--	2.84	67.7	0.49
S-81-HT1	Air	108	1	1.90	69.1	0.33
S-81-HT2	H ₂ O	108	2	10.34	49.4	1.8
S-81-HT3	[H ₂ O	108	2	2.93	62.9	0.51
	[followed by Air	108	1			
S-81-HT4	[Air	108	1	11.43	51.1	2.0
	[followed by H ₂ O	108	2			
S-81-HT5	Toluene	110	2	2.40	67.3	0.42
S-81-HT6	[Air	108	1	2.82	65.0	0.49
	[followed by Toluene	110	2			
S-81-HT7	[Toluene	110	2	1.78	72.9	0.31
	[followed by Air	108	1			

TABLE 15. TRANSPORT PROPERTIES OF COGRAFTED
POLYETHYLENE MEMBRANES

Film No.	Monomer Concentration, wt %*			Flux, Gfd	Salt Rejection %	Membrane Constant A x 10 ⁵ cm ³ /cm ² sec Atm
	Acrylic Acid	Vinyl Acetate	Acrylonitrile			
S-85	5	20	--	3.86	61.5	0.67
S-86	10	15	--	3.22	64.9	0.56
S-87	15	10	--	5.62	60.8	0.98
S-88	20	5	--	3.62	66.2	0.63
S-89	20	--	5	5.62	58.4	0.98
S-90	15	--	10	5.26	60.0	0.92
S-91	10	--	15	5.75	60.7	1.0
S-92	5	--	20	2.93	63.7	0.51

* Benzene solvent, no terminator with vinyl acetate, 5 wt % CCl₄ terminator with acrylonitrile.

The acrylic acid-vinyl acetate series shows flux values of 3.22 to 5.62 gfd, with salt rejections of 60.8 to 66.2%. The membrane constants are relatively constant at about $0.6 \times 10^{-5} \text{ cm}^3/\text{cm}^2\text{sec Atm}$, except for film S-87, where the value was 0.98×10^{-5} .

For the acrylic acid-acrylonitrile series, flux values were in the range of 2.93 to 5.75 gfd, with salt rejections of 58.4 to 63.7%, with membrane constants of 0.9 to 1.0×10^{-5} , except for film S-92, where the membrane constant was 0.5×10^{-5} . It is now believed that the rather uniform results obtained in both these series are a result of the washing procedure used subsequent to the grafting operation. To remove adherent and/or occluded homopolymer from the acrylic acid-grafted films, it is necessary to wash the grafted film in 5% aqueous potassium hydroxide at 95-97°C for one hour, followed by water washing to neutrality. It appears that this treatment was sufficiently vigorous to hydrolyze the major portion of the polyacrylonitrile or the poly(vinyl acetate) in the graft terpolymer. Such hydrolysis would give a poly(acrylic acid-vinyl alcohol) side chain in the case of the vinyl acetate-acrylic acid cograft, and a poly(acrylic acid) side chain in the case of the acrylonitrile-acrylic acid cograft. Incomplete hydrolysis in the latter case could result in incorporation of acrylamide moieties in the side chains. The modified side chains in these films may account for the relatively good salt rejection at the flux levels attained, as compared to standard acrylic acid grafted films.

Two series of styrene-acrylic acid cografted films were prepared. In both series, the total monomer concentration in the grafting solution was maintained at 25 wt % with the weight ratio of styrene to acrylic acid being varied from 4:1 to 1:4. One series was prepared utilizing 5 wt % carbon tetrachloride as a chain terminator, while the other series utilized no chain terminator. In the series with no chain terminator, the film prepared with 20 wt % styrene-5 wt % acrylic acid in the grafting solution could not be unrolled after grafting. It appeared that the polyethylene base stock had grafted solidly to the cheesecloth interleaving material.

The balance of the films in both series were successfully unrolled and separated from the interleaving material. Results obtained

on evaluation of these films are shown in Table 16. As can be seen for both series of films, the water flux appears to increase with increasing styrene content, except for film S-109 which does not support this trend. It should be mentioned that this trend of increasing water flux with increasing styrene content was contrary to expectations. It was also surprising that the films prepared without the use of chain terminator showed higher water flux values than films prepared with corresponding styrene-acrylic acid content in the grafting solutions with chain terminator added, except for the films prepared with 20 wt % acrylic acid solution. It had previously been shown that for straight acrylic acid-modified polyethylene films, variation of the chain terminator content of the grafting solution over the range of 0-12 wt % had no effect on transport properties.

As is usual with poly(acrylic acid)-containing films, the salt rejection in both series of films decreased as the water flux increased. However, films which were prepared with the highest acrylic acid content in the grafting solution had the highest salt rejection, which is opposed to the results usually obtained on straight acrylic acid-grafted films. Also worth noting is the fact that when salt rejection by films prepared with the same acrylic acid-styrene ratios in the grafting solution are compared between the two series, similar values are observed. This would seem to indicate that salt rejection is a function of poly(acrylic acid) content in these films.

A series of films was prepared by cograftering polyethylene with vinyltoluene-acrylic acid mixtures in the weight ratio of 4:1 to 1:4. These films were prepared without the use of a chain transfer agent. Two vinyltoluene-acrylic acid cografterings were prepared (2:1 and 3:2 weight ratio VT/AA) utilizing 5 wt % carbon tetrachloride in the grafting solution to determine the effect of chain transfer agent with this system. The data obtained upon evaluation of these films are shown in Table 17.

For styrene-acrylic acid grafted films described above, a trend of increasing flux with increasing styrene content was observed. From the data presented in Table 17, it can be seen that similar results were obtained; as the vinyltoluene content increased, water flux increased. The salt rejections for these films decrease with increasing vinyltoluene content except for film S-127, similar to the trend

TABLE 16. TRANSPORT PROPERTIES OF SOME ACRYLIC
ACID-STYRENE COGRAFTED MEMBRANES

Film No.	Grafting Solution		Flux, Gfd	Salt Rejection %	Membrane Constant A ² x 10 ⁵	Film Wet Thickness, mils
	Acrylic Acid	Styrene wt % ¹				
S-97	10	15	-- 8.82	53.3	1.52	2.0
S-98	15	10	-- 7.14	54.7	1.23	2.1
S-99	20	5	-- 3.48	61.5	0.60	2.0
S-107	20	5	5 4.34	59.2	0.75	1.4
S-108	15	10	5 5.07	54.9	0.88	1.1
S-109	10	15	5 4.03	52.1	0.70	1.1
S-110	5	20	5 8.69	45.2	1.51	1.5

¹ All grafting reactions utilized benzene solvent.

² cm³/cm² sec Atm.

TABLE 17. TRANSPORT PROPERTIES OF SOME ACRYLIC
ACID-VINYLTOLUENE COGRAFTED
POLYETHYLENE MEMBRANES

Film No.	Grafting Solution Composition, wt %			Flux, ¹ Gfd	Salt Rejection ¹ %	Membrane Constant ² A x 10 ⁵
	Acrylic Acid	Vinyl- toluene	CCl ₄			
S-116	5	20	--	8.42	59.4	1.45
S-115	10	15	--	8.37	62.9	1.44
S-127	15	10	--	5.70	57.0	0.97
S-126	20	5	--	3.15	64.5	0.53
S-117	15	10	5	1.34	66.4	0.23
S-128	20	5	5	2.62	64.0	0.45

¹ Measured at 400 psig with 0.25 wt % saline.

² cm³/cm² sec Atm.

observed with the styrene-acrylic acid cografterd materials. The two vinyltoluene-acrylic acid films prepared with chain transfer agent both show lower flux than their counterpart films prepared without chain transfer agent, while film S-117 has a higher salt rejection than S-127, and film S-128 has essentially the same rejection as S-126. This may reflect a lower degree of grafting with the vinyltoluene-acrylic acid system when used with a chain transfer agent, although no such effect was noted with straight acrylic acid-grafted films.

Chemical modification of acrylic acid-grafted polyethylene film subsequent to the grafting operation was tried to determine the effect on transport properties. Film S-83 was utilized, since the free acid form showed a relatively good water transport of 3.14 gfd with a salt rejection of 65.7% (Table 18). Neutralization of this film with potassium hydroxide produced a film with a water flux of 2.48 gfd and a salt rejection of 69%. This behavior was somewhat unusual, since the potassium salt form of acrylic acid-grafted films normally shows higher flux values and lower salt rejection than the free acid forms. This film was allowed to react with a methanolic solution of poly(4-vinylpyridine) to form a polysalt layer on both surfaces of the film. This polysalt membrane gave salt rejection of 82.7% at a water flux of 1.24 gfd. The increase in salt rejection obtained indicates that chemical modification of the surface of acrylic acid films could lead to improved membranes. This film was evaluated at several pressures, as shown in Table 19. While the flux increased from 1.24 to 1.84 gfd on going from 400 to 800 psig feed pressure, a decrease in the membrane constant A from 0.213×10^{-5} to 0.160×10^{-5} indicated that some membrane compression under the increased hydraulic loading was occurring, as has been observed before with grafted films. A modest increase in salt rejection from 82.7 to 84.3% was observed as the pressure was increased.

Further chemical modification of films after grafting was performed on several films. Film S-81, which was prepared using 25 wt % acrylic acid in the grafting solution, was evaluated as the free acid, the potassium salt, and the n-octylamine salt, with the results shown in Table 20. The free acid form of the film showed 2.23 gfd water flux and 70.0% salt rejection. The relatively more hydrophilic

TABLE 18. CHEMICAL MODIFICATION OF GRAFTED
POLYETHYLENE FILM¹ -- EFFECT ON
TRANSPORT PROPERTIES

Chemical Treatment	Nature of Poly(acrylic acid) Side Chain	Flux, ² Gfd	Salt Rejection %	Membrane Constant A x 10 ⁵ cm ³ /cm ² sec Atm
None	Free Acid	3.14	65.7	0.54
Neutraliza- tion with 5% KOH	Potassium salt	2.48	69.0	0.43
Neutraliza- tion with methanolic solution of poly(4-vinyl pyridine)	Polysalt layer at surface of film	1.24	82.7	0.21

¹ Film S-83, grafted with 15 wt % acrylic acid in benzene, 3% CCl₄ terminator.

² Feed - 0.25 wt % saline, 400 psig.

TABLE 19. CHEMICALLY MODIFIED FILM -- RESULTS
AT VARIOUS OPERATING PRESSURES

S-83-Polysalt ¹			
Pressure Atm	Flux, ² Gfd	Salt Rejection %	Membrane Constant A x 10 ⁵ cm ³ /cm ² sec Atm
27.2	1.24	82.7	0.213
40.8	1.55	83.3	0.179
54.5	1.84	84.3	0.160

¹ Poly(acrylic acid)-grafted film, free acid form reacted with poly(4-vinylpyridine).

² Feed -- 0.25 wt % saline.

TABLE 20. CHEMICAL TREATMENT OF GRAFTED FILMS --
EFFECT ON TRANSPORT PROPERTIES

Film No.	Treatment	Flux, Gfd	Salt Rejection %	Membrane Constant A x 10 ⁵ cm ³ /cm ² sec Atm
S-81	Acrylic acid graft as potassium salt	2.84	67.7	0.49
S-81	Acrylic acid graft as free acid	2.23	70.0	0.38
S-81	Acrylic acid graft as n-octylamine salt	1.55	70.8	0.27
S-110	Styrene-acrylic acid cograft as potassium salt	8.69	45.2	1.51
S-110-S	Styrene-acrylic acid graft - sulfonated at 90-100°C, as potassium salt	1.62	59.7	0.28
S-83	Acrylic acid graft as potassium salt	2.48	69.0	0.43
S-83-A	Acrylic acid graft 1 hr at 98-100°C in .007M NaOCl as potassium salt	3.96	61.1	0.68
S-83-B	Acrylic acid graft 2 hr at 98-100°C in .007M NaOCl as potassium salt	3.30	59.5	0.57
S-83-C	Acrylic acid graft 3 hr at 98-100°C in .007M NaOCl as potassium salt	2.55	59.2	0.44

potassium salt had a higher water flux (2.84 gfd) and a lower salt rejection (67.7%). It was thought that an amine salt with a large hydrocarbon substituent might reduce the hydrophilicity, giving higher salt rejection. The n-octylamine salt of S-81 showed a relatively low water flux of 1.55 gfd and a salt rejection of 70.8%, not appreciably better than the free acid form.

A styrene-acrylic acid cografted film (S-110) with a flux of 8.69 gfd and a salt rejection of 45.2% was sulfonated by heating in concentrated sulfuric acid for 30 minutes at 90-100°C. That some polymer degradation occurred during the sulfonation was evidenced by a 24% weight loss during the reaction. The sulfonated film (S-110-S) showed a low water flux of 1.62 gfd and a salt rejection of 59.7%, possibly indicating that any gain in performance due to introduction of the sulfonic acid groups was at least partially offset by polymer degradation.

Finally, three specimens of film S-83 were treated in 0.007 molar sodium hypochlorite solution at 98-100°C for one, two and three hours, respectively. This treatment results in a progressive decrease in the poly(acrylic acid) content of the graft copolymer, as evidenced by a decrease in the intensity of the absorption peak for the carboxyl group in the infrared spectra of these treated films. These films all showed an increase in water flux and a decrease in salt rejection compared to the untreated film, as shown in Table 20. The highest flux and salt rejection among the treated films were observed for the film treated for one hour, with both flux and salt rejection continuing to decrease upon further treatment. These results are somewhat unusual in that changes in grafted films that lead to decrease in water flux usually lead to increases in salt rejection.

Efforts to reduce the hydrophilicity of acrylic acid-grafted films by cografting acrylic acid in admixture with a crosslinking agent were made. The films prepared and the data obtained upon their evaluation are shown in Table 21.

As can be seen, increase in the concentration of divinylbenzene in the grafting solution from 5 wt % (S-80) to 10 wt % (S-122) and 15 wt % (S-123) led to progressively lower water fluxes, which

TABLE 21. CROSSLINKED ACRYLIC ACID-
GRAFTED MEMBRANES

Film No.	Grafting Solution Composition, wt %		Flux, ¹ Gfd	Salt Rejection ¹ %	Membrane Constant ² A x 10 ⁵
	Acrylic Acid	Crosslinking Agent			
S-80	25	Divinylbenzene	5 1.17	79.8	0.202
S-122	25	Divinylbenzene	10 0.62	71.0	0.103
S-123	25	Divinylbenzene	15 0.21	71.0	0.036
S-129	15	Divinylsulfone	10 2.76	67.4	0.480
S-130 ³	15	Ethylene glycol dimethacrylate	10 0.47	80.3	0.080

¹ Measured at 400 psig with 0.25 wt % saline.

² cm³/cm² sec Atm.

³ Film as free acid.

was expected. However, salt rejection did not increase as was expected but decreased from 79.8% for film S-80 to 71.0% for both S-122 and S-123. A film (S-129) prepared with 15 wt % acrylic acid and 10 wt % divinylsulfone showed a water flux of 2.76 gfd and a salt rejection of 67.4%, not markedly different from the corresponding values of 2.48 gfd and 69.0% obtained for film S-83 which was prepared with 15 wt % acrylic acid in the grafting solution. The use of ethylene glycol dimethacrylate (10 wt %) with acrylic acid (15 wt %) produced a film (S-130) which displayed a low water flux of 0.47 gfd and a salt rejection of 80.3%.

The two crosslinked membranes which showed the best salt rejections (S-80 and S-130) were evaluated at several operating pressures (Table 22). Film S-80 was prepared by grafting with acrylic acid in admixture with 5% divinylbenzene. The flux for this film remained relatively constant over the range of 400 to 800 psig, while the membrane constant decreased, indicating membrane compression due to loss of imbibed water. As the pressure was increased, the salt rejection increased from 79.8 to 85%. While the water flux was relatively low, the salt rejection was superior to that observed for non-crosslinked membranes at about the same flux levels (i.e., 1.13 gfd, 67.5% salt rejection).

Film S-130, which was prepared with 10% ethylene glycol dimethacrylate as a crosslinking agent, was evaluated in the potassium salt form at pressures up to 68.2 atmospheres. Flux increased over the range of pressure studied, while the membrane constant decreased slightly, again indicating some compression of the membrane. This membrane in the potassium salt form showed higher flux (1.07 gfd) and lower salt rejection (58.9%) than the same film as the free acid (0.47 gfd and 80.3%, respectively). However, the potassium salt form of this membrane showed better than average resistance to compression compared to the average acrylic acid-grafted membrane, with the membrane constant decreasing only 18.9% over the range of 27.2 to 68.2 atmospheres, while uncross-linked membranes show membrane constant decreases of over 50% over the same pressure range. The salt rejection rose sharply from 58.9% at 27.2 atmospheres to 85.5% at 68.2 atmospheres. The

TABLE 22. CROSSLINKED ACRYLIC ACID-GRAFTED FILMS --
RESULTS AT VARIOUS PRESSURES

P Atm.	S-80 ¹			S-130 ²		
	Flux, ³ Gfd	Salt Rejection %	Membrane Constant A ⁴ x 10 ⁵	Flux, ³ Gfd	Salt Rejection %	Membrane Constant A ⁴ x 10 ⁵
27.2	1.17	79.8	0.202	1.07	58.9	0.185
40.8	1.02	82.7	0.117	1.52	69.5	0.176
54.5	1.19	85.0	0.103	---	---	---
68.2	---	---	---	2.16	85.5	0.150

¹ Acrylic acid-grafted membrane, crosslinked with 5% divinylbenzene during grafting. Film as potassium salt.

² Acrylic acid-grafted membrane, crosslinked with 10% ethylene glycol dimethacrylate during grafting. Film as potassium salt.

³ 0.25 wt % saline feed.

⁴ cm³/cm².sec Atm.

favorable results obtained with the ethylene glycol dimethacrylate crosslinked film indicate that polyfunctional unsaturated esters may be superior crosslinking agents, as compared difunctional hydrocarbon-type compounds such as divinylbenzene.

V. CONCLUSIONS AND RECOMMENDATIONS

A variety of monomers were used to modify polyolefin film by irradiation grafting techniques to give hydrophilic water permeable membranes. It was found that highly hydrophilic films imbibe large amounts of water and assume a swollen gel-like structure. The large amounts of water in these films lead to water transport by viscous flow, and a resulting highly coupled salt flow.

Attempts to reduce the hydrophilicity of grafted polyethylene films by forming graft terpolymers with mixtures of hydrophilic and hydrophobic monomers, or mixtures of hydrophilic monomers with crosslinking agents, led to membranes with enhanced salt rejection but with reduced water flux. Similar results were obtained by further chemical modification of grafted polyethylene films subsequent to the grafting step.

In view of the results outlined above, it is recommended that future work be directed toward preparation of modified polyolefin films with high salt rejection, possibly at the expense of reduced water flux. Approaches to preparing these materials should involve preparation of graft terpolymers using hydrophilic-hydrophobic monomer mixtures, hydrophilic monomer-crosslinking agent mixtures, or post-grafting chemical treatment. Those procedures which provide the best membranes from the standpoint of salt rejection should then be utilized to prepare modified small, hollow polyolefin fibers, where the low flux values per unit area one would expect for high rejection grafted membranes can be overcome due to the large surface area available with hollow membrane reverse osmosis modules.

VI. REFERENCES

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